

5 SELECTIVE HYDROGENATION CATALYST

Background of Invention

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This invention relates to a catalyst useful for selective hydrogenation of unsaturated compounds, such as acetylene, in an olefinic feed stream, particularly for front-end ethylene purification. This invention also 15 relates to a process for the preparation of the catalyst and the use of the catalyst for the selective hydrogenation of unsaturated compounds, such as acetylene, particularly for front-end ethylene purification.

The manufacture of unsaturated hydrocarbons usually 20 involves cracking various types of hydrocarbons and often produces a crude product containing hydrocarbon impurities that are more unsaturated than the desired product. These unsaturated hydrocarbon impurities are often very difficult to separate by fractionation from the desired 25 product. An example of this problem occurs with ethylene purification, in which acetylene is a common impurity. It is often difficult, industrially, to remove undesirable, highly unsaturated hydrocarbons by hydrogenation without significant hydrogenation of the desired hydrocarbons.

30 Two general types of gas phase selective hydrogenation processes for removing undesired, unsaturated hydrocarbons are commonly used. One type, known as "front-end" hydrogenation, involves passing the

5 crude gas from the initial cracking step, after removal of
steam and condensable organic material, over a
hydrogenation catalyst. The crude gas has a large
hydrogen content relative to the quantity of acetylenes
present, thereby, theoretically making possible the
10 hydrogenation of all of those acetylenes as well as a
substantial quantity of the ethylene that is present. In
practice, substantially complete hydrogenation of the
acetylenes with sufficient selectivity to produce olefins
of polymerization quality is often a problem. The high
15 concentration of hydrogen present in the front-end systems
results in the need for a very selective catalyst that
does not also substantially hydrogenate desirable
components of the feed stream, such as ethylene.
Overhydrogenation can lead to a thermal excursion in
20 reactors, which is also known as "run-away". Under
"run-away" conditions, excessively high temperatures are
experienced, severe loss of ethylene occurs, and catalyst
damage takes place. Another problem that can occur in a
front-end reactor system is a furnace upset which can
25 result in swings in the CO concentration from moderate
levels to very low levels. Conventional, front-end
catalysts cannot tolerate these large swings in CO
concentration very well which often produce "run-away"
conditions.

30 In the other type of gas phase selective
hydrogenation, which is known as "tail-end" hydrogenation,

5 the crude gas is first fractionated and the resulting concentrated product streams are individually reacted with hydrogen in a slight excess over the quantity required for hydrogenation of the undesirable, highly unsaturated hydrocarbons, such as acetylene. However, in tail-end
10 processes there is a greater tendency for deactivation of the catalyst, and consequently, periodic regeneration is necessary. While thermal excursion is not a concern, formation of undesirable polymers is often a major problem.

15 A number of patents have discussed selective hydrogenation of unsaturated hydrocarbons, such as U.S. Patent Nos. 4,126,645, 4,367,353, 4,329,530, 4,347,392 and 5,414,170. The catalysts that are preferred for selective hydrogenation reactions conventionally utilize palladium,
20 supported on an alumina substrate, as disclosed, for example, in U.S. Patent Nos. 3,113,980, 4,126,645 and 4,329,530. Other gas phase, palladium on alumina catalysts for the selective hydrogenation of acetylene compounds are disclosed, for example, in U.S. Patent Nos.
25 5,925,799, 5,889,138 and 5,648,576.

One of the problems with conventional palladium on alumina catalysts is that under normal operating conditions not only is the acetylene hydrogenated, a substantial proportion of the ethylene is also converted
30 to ethane. In addition, the palladium on alumina catalysts often have relatively low stability due to the

5 formation of large quantities of oligomers on the catalyst surface during the selective hydrogenation process.

To overcome these problems, promoters or enhancers are added to the catalyst. One common enhancer for a conventional palladium on alumina selective hydrogenation 10 catalysts is silver. Acetylene hydrogenation catalysts for ethylene purification comprising palladium and silver on a support material are disclosed in U.S. Patent Nos. 4,404,124, 4,484,015, 5,488,024, 5,489,565 and 5,648,576.

Catalysts comprising palladium, silver, an alkali 15 metal fluoride and a support material, which are utilized for the hydrogenation of feed stream impurities, such as dienes and diolefins, are disclosed, for example, in U.S. Patent No. 5,489,565.

Catalysts useful for hydrogenation of organic 20 compounds are also disclosed in U.S. Patent Nos. 6,255,548 and 6,294,696 and comprise at least one support, at least one metal from Group VIII, and at least one additional element, M, selected from the group consisting of germanium, tin, lead, rhenium, gallium, indium, gold, 25 silver and thallium, preferably tin or germanium. The catalyst for this process is prepared by introducing a metal into an aqueous solvent, preferable in the form of an organometallic compound containing at least one carbon-M bond. See also U.S. Patent Nos. 3,962,139 and 30 6,225,516.

5 U.S. Patent No. 6,465,391 discloses a selective
hydrogenation catalyst and processes for the production
thereof, wherein the catalyst comprises an inorganic
support material, a palladium component, a silver
component, and a promoter component having the formula
10 XYFn, where an X is an alkaline metal, Y is an element
selected from the group consisting of antimony,
phosphorous, boron, gallium, aluminum, indium, thallium,
and arsenic and n is an integer which makes YFn an
monovalent anion.

15 U.S. Patent No. 3,992,468 discloses a process for
hydrodealkylating alkylaromatic hydrocarbons using a
catalyst comprising two metals, the first of the metals
selected from the group consisting of cobalt, ruthenium,
osmium, palladium, rhodium, indium, and platinum or from
20 the group consisting of molybdenum, tungsten, and
manganese, and the second metal selected from the group
consisting of zinc, cadmium, gallium, indium, thallium,
manganese, copper, silver, gold, yttrium, titanium,
niobium, tantalum, chromium, molybdenum, tungsten,
25 rhenium, germanium, tin and lead.

While conventional silver/palladium-based catalysts
for the selective hydrogenation of acetylene have been
useful, there are a number of problems that have been
discovered from their use, including relatively low
30 tolerance to carbon monoxide concentration swings and
lower selectivity than is desirable by the industry.

5 The catalysts of the invention are designed to
address these deficiencies in conventional ethylene
purification catalysts.

Accordingly, it is an object of this invention to
disclose a process for the selective hydrogenation of an
10 olefinic feed stream containing acetylenic impurities,
particularly for ethylene purification.

It is a further object of this invention to disclose
a process for front-end selective hydrogenation of
acetylenic impurities, whereby the quantity of the
15 desirable olefins, particularly ethylene, is not
substantially reduced.

It is a further object of the invention to disclose a
palladium/thallium catalyst for use in the selective
hydrogenation of acetylenic impurities, particularly for
20 use in front-end ethylene purification.

It is a further object of the invention to disclose a
palladium/thallium catalyst for selective hydrogenation of
acetylenic impurities which contains precise quantities of
palladium and thallium.

25 It is a still further object of the invention to
disclose a palladium/thallium selective hydrogenation
catalyst for the selective hydrogenation of acetylene
which exhibits improved selectivity, resistance to
run-away, and tolerance to CO concentration swings in
30 comparison with conventional palladium or palladium/silver
selective hydrogenation catalysts.

5 These and other objects can be obtained by the
disclosed selective hydrogenation catalyst and process for
the preparation and use of the selective hydrogenation
catalyst for use in an olefinic feed stream containing
acetylenic impurities, particularly for ethylene
10 purification.

Summary of the Invention

The present invention is a process for the production
and distribution of a catalyst for the selective
15 hydrogenation of acetylenic impurities for ethylene
purification comprising

preparing a carrier material in a suitable shape;
impregnating the carrier with a palladium metal
source, preferably in solution;
20 calcining the palladium-impregnated carrier;
impregnating the palladium-impregnated carrier with a
thallium- metal source, preferably in solution,
calcining the palladium/thallium impregnated carrier;
and
25 reducing the palladium and thallium materials, wherein
the quantity of the reduced palladium, by weight,
including the palladium, comprises from about 0.001 to
about 2 weight percent, the quantity of the reduced
thallium, by weight including the thallium, comprises from
30 about 0.001 to about 1 weight percent and wherein the

5 concentration of the palladium metal is not less than the concentration of the thallium metal.

Preferably the reduced catalyst is then sealed into shipping containers under a non-oxidizing material for shipment.

10 The present invention further comprises a palladium/thallium catalyst for front-end selective hydrogenation of acetylenic impurities comprising from about 0.001 to about 2 weight percent palladium, including the palladium, and from about 0.001 to about 1 weight percent thallium, including the thallium, on a low surface area carrier i.e. less than 100 m²/g, wherein the concentration of the palladium metal is not less than the concentration of the thallium metal. Preferably the ratio of the palladium metal to the thallium metal is 1:1 or 15 less, more preferably about 10:1 or less.

20 The invention further comprises a process for the selective hydrogenation of acetylenic impurities for front-end ethylene purification comprising passing an ethylene feed stream containing acetylenic impurities over 25 the catalyst described above.

Detailed Description

The catalyst of the invention is designed primarily for the selective hydrogenation of acetylene in admixture 30 with ethylene, particularly for front-end processes. The feed stream for this selective hydrogenation process

5 normally includes substantial quantities of hydrogen,
methane, ethane, ethylene, small quantities of carbon
monoxide and carbon dioxide, as well as various
impurities, such as acetylene. The goal of the selective
hydrogenation process is to reduce substantially the
10 amount of the acetylenic impurities present in the feed
stream without substantially reducing the amount of
ethylene that is present. If substantial hydrogenation of
the ethylene occurs, thermal run-away can occur which
adversely affects the catalyst. The catalyst of the
15 invention exhibits enhanced selectivity, resistance to
run-away, and better tolerance for CO concentration swings
than is experienced using conventional selective
hydrogenation catalysts.

The catalyst that is useful for this selective
20 hydrogenation process is comprised of a low surface area
carrier into which palladium and thallium are impregnated.
The catalyst carrier is any relatively low surface area
catalyst carrier manufactured from alumina, alpha alumina,
zinc oxide, nickel spinel, titania, magnesium oxide,
25 cerium oxide and mixtures thereof. In a preferred
embodiment, the catalyst carrier is an alpha alumina. The
surface area of the catalyst carrier is preferably from
about 1 to about 100 m²/g, more preferably from about 1 to
about 50 m²/g, and most preferably from about 1 to about 10
30 m²/g. Its pore volume is from about 0.2 to about 0.7 cc/g,
preferably from about 0.3 to about 0.5 cc/g.

5 The catalyst carrier can be formed in any suitable
size and in any suitable shape, such as spherical,
cylindrical, trihole trilobal, monolith, pellet, tablet,
ring and the like. In a preferred embodiment the catalyst
carrier is formed in a tablet shape with a diameter from
10 about 3 to about 5 mm.

Palladium can be introduced into the catalyst carrier
by any conventional procedure. The presently preferred
technique involves impregnating the catalyst carrier with
a palladium metal source, preferably in the form of an
15 aqueous solution of a palladium salt, such as palladium
chloride or palladium nitrate, preferably palladium
chloride. The extent of penetration of the palladium salt
is preferably controlled by adjustment of the pH of the
solution. In a preferred embodiment, the depth of
20 penetration of the palladium salt is controlled such that
approximately 90 percent of the palladium salt is
contained within about 250 microns of the surface of the
catalyst carrier. Any suitable method can be used to
determine palladium penetration, such as is disclosed in
25 U.S. Patent Nos. 4,484,015 and 4,404,124. After palladium
impregnation, the intermediate impregnated catalyst
composition is calcined at a temperature from about 400°C
to about 600°C for at least one hour.

Once the palladium-impregnated intermediate catalyst
30 composition has been calcined, that composition is further
impregnated with a thallium metal source, preferably a

5 thallium metal solution such as HCO₂Tl. The
10 palladium/thallium impregnated catalyst material is then
calcined at a temperature from about 400°C to about 600°C
for at least one hour.

In an alternative process of manufacture, the
15 thallium and palladium metals can be co-impregnated and
then calcined. Notwithstanding, it is preferable that
thallium metal source not be introduced before the source
for the palladium metal.

While the reduction process can occur *in situ* within
15 a front-end reactor, the metals of the catalyst are
preferably reduced in a reduction furnace prior to
shipment. The metal compounds contained in the
thallium/palladium catalyst precursor are preferably
reduced by heating the catalyst while under a reducing
20 gas, at a temperature from about 94°C - 535°C, preferably
from about 94°C - 260°C for a time sufficient to reduce
the palladium and thallium metal sources. Preferable
reducing gases include hydrogen, carbon monoxide and
mixtures thereof. The catalyst is then cooled under a
25 purge gas, such as nitrogen, to room temperature. Other
conventional reduction processes may alternatively be
used.

The amount of palladium present after reduction is
from about 0.001 to about 2 weight percent, preferably
30 from about 0.005 to about 0.05 weight percent, and most
preferably from about 0.01 to about 0.03 weight percent

5 based on the total weight of the catalyst, including the palladium. The amount of thallium present in the catalyst after reduction is from about 0.001 to about 1 percent, preferably 0.001 to 0.03 weight percent, and most preferably from about 0.001 to about 0.01 weight percent,
10 based on the total weight of the catalyst, including the thallium.

It has been discovered that a useful catalyst is produced when the concentration of palladium metal equals or exceeds the concentration of thallium metal with a
15 preferable Pd:Tl ratio from 1:1 to about 100:1, a more preferable Pd:Tl ratio from 5:1 to about 50:1, and a most preferable Pd:Tl ratio from about 10:1 to about 20:1, calculated as metals.

Following a final drying step, the thallium/palladium
20 containing catalyst is prepared for shipment. The catalyst is preferably loaded into individual containers under a non-oxidizing gaseous atmosphere for shipping. Preferable non-oxidizing gases include nitrogen, argon, carbon dioxide or mixtures thereof.

25 In use, the catalyst is placed in the bed of a reactor. If desired the catalyst can be reduced *in situ* as is possible in some operations. Alternatively, the catalyst, which has been reduced prior to shipment, is merely placed within a catalyst bed ready for use.
30 Selective hydrogenation of acetylene occurs when a gas stream containing primarily hydrogen, ethylene, methane,

5 unsaturated impurities, such as acetylene, and minor amounts of carbon monoxide is passed over the catalyst of the invention. The inlet temperature of the feed stream is raised to a level sufficient to hydrogenate the acetylene. Generally, this temperature range is about
10 35°C to about 100°C. Any suitable reaction pressure can be used. Generally, the total pressure is in the range of about 100 to 1000 psig with the gas hourly space velocity (GHSV) in the range of about 1000 to about 14000 liters per liter of catalyst per hour.

15 Conventional palladium/silver catalysts are often prone to run-away conditions, especially when the quantity of carbon monoxide changes dramatically during the reaction process. The catalyst of the invention is resistant to these run away conditions even when the
20 quantity of carbon monoxide is low. Further, the catalyst of the invention exhibits enhanced selectivity over prior art catalysts. By the process of use of the catalyst of the invention, reduction of acetylene to a level less than about 1 ppm can be achieved.

25 Regeneration of the catalyst may be accomplished by heating the catalyst in air at a temperature, preferably not in excess of 500°C., to burn off any organic material, polymers or char.

30 **EXAMPLES**

Example 1 (Comparative)

5 A commercially available, palladium/alumina catalyst
manufactured by Süd-Chemie Inc. under the product name
G-83A is obtained. Analysis shows that the catalyst
comprises a palladium on alumina catalyst containing 0.018
weight percent palladium. The carrier is comprised of 99
10 weight percent alumina. The catalyst has a BET surface
area of 3.7 m²/g.

Example 2 (Comparative)

A commercially available catalyst manufactured by
15 Süd-Chemie Inc. under the product name of G-83C is
obtained. Analysis shows that the catalyst comprises a
palladium/silver on alumina catalyst containing 0.018
weight percent of palladium and 0.07 weight percent of
silver on 99 weight percent alumina. The catalyst has a
20 BET surface area of about 4.3 m²/g.

Example 3

A catalyst is prepared by dipping 100 grams of a
commercially available, low surface area alumina spheres
25 with a BET surface area of 50 m²/g in a PdCl₂ solution to
yield a palladium loading of 0.03 weight percent,
including the palladium, with a palladium depth of
penetration that is controlled to wherein at least about
90 percent of the palladium is within 250 microns of the
30 surface of the spheres. After palladium impregnation, the
intermediate catalyst is calcined at 454°C for 3 hours.

5 The palladium-containing intermediate is then impregnated
with thallium in the form of HCO₂Tl to yield a thallium
loading of 0.03 weight percent, including the thallium.
The weight ratio between the palladium metal and the
thallium metal on a by weight basis is 1:1. The catalyst
10 containing the palladium and thallium is calcined a second
time at about 454°C for 3 hours. The catalyst is then
loaded into a reduction bed, and purged with nitrogen
while the bed is heated to 94°C. Once this temperature is
reached, the nitrogen purge gas is discontinued and
15 hydrogen gas is introduced as a reducing gas. The bed is
maintained at 94°C for at least 60 minutes. Upon
completion of the reduction cycle, nitrogen gas is
reintroduced into the bed and the bed is cooled to room
temperature.

20

Example 4

A catalyst is prepared according to Example 3 except
the low surface area alumina has a BET surface area of 5
m²/g. The catalyst is then loaded into a reduction bed,
25 purged with nitrogen while the bed is heated to 94°C, and
reduced as described in Example 3.

Example 5

A catalyst is prepared according to Example 3 except
30 the weight ratio between the palladium metal and thallium
metal was 10:1 Pd:Tl (0.03 weight percent palladium,

5 including the palladium, and 0.003 weight percent
thallium, including the thallium). Further, the catalyst
is not reduced.

Example 6

10 The catalyst from Example 5 is reduced as described
in Example 3.

Example 7

A catalyst is prepared according to Example 6 except
15 that the low surface area alumina has a BET surface area
of 5m²/g.

TABLES

Performance Testing:

20 Table 1, which follows, provides a comparison of the
performance of Examples 1 and 2 (Comparative Examples)
with Examples 3 through 7. The samples are compared by
passing a conventional ethylene feed stream over the
catalysts. The catalysts are evaluated in a bench scale
25 laboratory, one-half inch i.d. reactor tube, which
simulated a front-end feed stock reactor.

Catalyst activity and selectivity are evaluated. For
each catalyst, the inlet temperature is recorded when less
than 25 ppm acetylene leakage is detected at the reactor
30 outlet. This temperature, T₁, is designated as the lower
reaction temperature for catalyst activity. The inlet

5 temperature is then increased until "run-away" is observed. "Run-away" or thermal excursion is defined as a greater than 4 percent H₂ loss in the system, and occurs when the hydrogenation of ethylene (C₂H₄) is significant.
10 noted is reported as T₂. The catalyst activity then is evaluated in terms of the temperature range over which the catalyst could effectively function, or the temperature at which hydrogenation is first observed (T₁) to the temperature at which run-away occurs (T₂). A large delta T
15 (T₂-T₁) indicates that the catalyst can operate effectively over a broad temperature range.

As the reactor temperature is increased, the hydrogenation reaction becomes more active with a greater amount of C₂H₂ being hydrogenated and hence, removed from
20 the product stream. However, some hydrogenation of C₂H₄ also occurs indicating a loss of selectivity for the reaction. As shown in Table I, "selectivity" of each catalyst is reported as a percentage and is determined by the following calculations: 100 times (inlet C₂H₂ - outlet
25 C₂H₂) minus (C₂H₄ outlet minus C₂H₄ inlet)/(C₂H₂ inlet minus C₂H₂ outlet) times 100. Higher positive percentages indicate a more selective catalyst. Data was obtained at a moderate GHSV (7000).

30 **TABLE I**

Table I - 7000 GHSV activity/selectivity test

5

Run	Catalyst	T ₁ (°C)	T ₂ (°C)	Activity Range T ₂ -T ₁	Selectivity at T ₁
Comparative Example 1	(G83A) Pd/Al ₂ O ₃ no pre-reduction	60	66	6	+3%
Comparative Example 2	(G83C) Pd/Ag/Al ₂ O ₃ no pre-reduction	46	52	6	-125%
Example 3	1:1 Pd:Tl (0.03%Pd, 0.03%Tl) on alumina 50 m ² /g S.A. (reduced)	46	58	12	-41.8%
Example 4	1:1 Pd:Tl (0.03%Pd, 0.03%Tl) on alumina 5 m ² /g S.A. (reduced)	37	57	20	+34%
Example 5	10:1 Pd:Tl (0.03%Pd, 0.003% Tl) on alumina (50 m ² /g S.A.) (No pre-reduction)	44	58	14	+46.6%
Example 6	10:1 Pd:Tl (0.03%Pd, 0.003%Tl) on alumina (50 m ² /g S.A.) (reduced)	67	84	17	+79%
Example 7	10:1 Pd:Tl (0.03%Pd, 0.003%Tl) on alumina (5 m ² /g S.A.) (reduced)	58	77	19	+41.7%

10 Comparison of the activity range and the selectivity for the prior art catalysts (Examples 1 - 2) to the inventive catalysts (Examples 3 - 7) demonstrates the enhanced performance of the catalysts of the invention. Selectivity is significantly improved relative to the 15 prior art catalysts. Further, the catalysts of the invention demonstrate a broader temperature range over which the catalysts are active for hydrogenation than the prior art catalysts.

20 CO concentration swings

Feedstreams supplied to commercial front-end hydrogenation reactors can have substantial swings in CO concentration. This occurs when a new hydrocarbon cracker is brought on-line. The CO present in the feedstream acts

5 as a selectivity enhancer. If the quantity of CO drops dramatically, thermal excursion can occur with existing commercial catalyst. To predict the performance of the catalysts of the invention under this condition, a test was developed to mimic CO concentration swings which often
10 occur in ethylene plants. Selected catalysts are tested under CO swing test conditions. The feed consists of 0.25% C₂H₂, 20% H₂, 247 ppm CO, 45% C₂H₄ and 34% CH₄. The temperature was increased until the reactor exit C₂H₂ levels reached 97% conversion. The CO level was then
15 reduced by a mass flow controller to 100 ppm. Test results are summarized in Table II.

Table II

Catalyst	Comparative Example 2		Example 7	
Pre-reduced	No		Yes	
CO level (ppm)	247	100	247	100
Temperature to reach ~97% conv. (°C)	43		44	
Conversion	98.1	Run-away	96.3	99.6
Selectivity @97% Conversion	-5.7	Run-away	29.9	-146.9

20

The catalyst of Example 7 showed enhanced selectivity
25 over the commercially available catalyst of Comparative Example 2. Thus the catalyst of the invention is more tolerant to CO reduction.

5 The principles, preferred embodiments, and modes of
operation of the present invention have been described in
the foregoing specification. The invention which is
intended to be protected herein, however, is not to be
construed or limited to the particular terms of
10 disclosure, as these are to be regarded as being
illustrative, rather than restrictive. Variations and
changes may be made by those skilled in the art without
departing from the invention.